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C668 C67X C699 C80Y C821
C4X X12 X12TP
U1S S1387

(56) Documents Cited

WO 95/16007 A1

(58) Field of Search

Online: CAS ONLINE

(54) Abstract Title

Polymerizable chiral dopants based on chiral tetrahydrofuran or hexahydrofuro[3,2-b]furan substituted by at least two mesogenic groups

(57) Chiral compounds are disclosed of the formula



where, independently of one another,

A is a spacer,

M is a mesogenic group containing two phenylene radicals which are unsubstituted or substituted by C₁- to C₄-alkyl, methoxy, ethoxy, fluorine, chlorine, bromine, C₁- to C₂₀-alkoxycarbonyl or C₁- to C₂₀-alkylcarbonyl and are linked via O, CO, OCO, OCOO or COO,

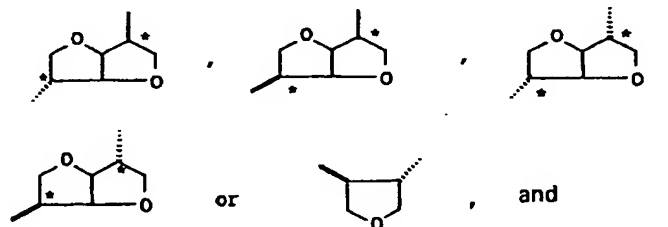
Y is a direct bond, O, S, COO, OCO, OCOO, CON(R) or N(R)CO, and

Z is a polymerizable group,

m is 0 or 1,

n is from 2 to 6, and

X is a chiral radical of the formula



R is C₁- to C₄-alkyl or hydrogen,

and their use as polymerizable, chiral high-twisting-power dopants for the production of cholesteric networks.

These compounds are suitable for use in electro-optical displays or as chiral dopants for nematic or cholesteric liquid crystals for producing layers which reflect in color. They may also be used as chiral dopants in optical polarizers and optical filters.

Polymerizable chiral compounds, and their use

- It is known that molecules which are anisotropic in shape can form liquid-crystalline phases, known as mesophases, on warming. The individual phases differ through the spatial arrangement of the major parts of the molecules on the one hand and through the molecular arrangement with respect to the long axes on the other hand (G.W. Gray, P.A. Winsor, *Liquid Crystals and Plastic Crystals*, Ellis Horwood Limited, Chichester 1974). The nematic liquid-crystalline phase is distinguished by the fact that there is only one alignment long-distance ordering due to the long molecular axes lining up in parallel. Under the prerequisite that the molecules making up the nematic phase are chiral, a cholesteric phase forms, in which the long axes of the molecules form a helical superstructure perpendicular thereto (H. Baessler, *Festkörperprobleme XI*, 1971). The chiral moiety may be present either in the liquid-crystalline molecule itself or added to the nematic phase as a dopant. Phases produced by doping are referred to as induced cholesteric phases. This phenomenon was first studied on cholesterol derivatives (H. Baessler, M.M. Labes, *J. Chem. Phys.* 52 (1970) 631; H. Baessler, T.M. Laronge, M.M. Labes, *J. Chem. Phys.* 51 (1969) 3213; H. Finkelmann, H. Stegemeyer, *Z. Naturforschg.* 28a (1973) 799). It later also became possible to induce cholesteric phases by adding other chiral substances which are not themselves liquid-crystalline (H. Stegemeyer, K.J. Mainusch, *Naturwiss.* 58 (1971) 599; H. Finkelmann, H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.* 78 (1974) 869).
- The cholesteric phase has remarkable optical properties: large optical rotation and pronounced circular dichroism caused by selective reflection of circular-polarized light within the cholesteric layer. The different colors observed depending on the veering angle depend on the pitch of the helical superstructure, which is itself dependent on the twisting power of the chiral component. The pitch and thus the wavelength range of the selectively reflected light of a cholesteric layer can be varied, in particular, by changing the concentration of a chiral dopant (J.E. Adams, W.E.L. Haas, *Mol. Cryst. Liq. Cryst.* 16 (1972) 33).
- Such cholesteric systems offer interesting opportunities for practical use. Thus, incorporation of chiral moieties into mesogenic acrylic esters after alignment in the cholesteric phase and photocrosslinking allows the production of a stable, colored network, but the concentration of the chiral component therein cannot be changed (G. Galli, M. Laus, A. Angeloni, *Makromol. Chem.* 187 (1986) 289). Furthermore, admixing of non-crosslinkable, chiral compounds with nematic acrylic esters

allows, after photocrosslinking, the production of a colored polymer (I. Heyndericks, D.J. Broer, Mol. Cryst. Liq. Cryst. 203 (1991) 113), but this still contains volatile constituents which are prohibitive for use.

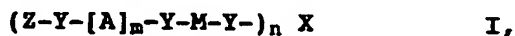
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EP-A-739403 describes chiral compounds which firstly have a high twisting power and secondly can be incorporated into the cholesteric phase in a stable manner in any desired concentration without diffusing or crystallizing out of the phase.

10

We have now found a group of compounds which has even better properties than those described above.

Accordingly, the present invention provides compounds of the
15 formula I



where, independently of one another,

20

A is a spacer,

M is a mesogenic group containing two phenylene radicals which are unsubstituted or substituted by C₁- to

25

C₄-alkyl, methoxy, ethoxy, fluorine, chlorine, bromine, C₁- to C₂₀-alkoxycarbonyl or C₁- to C₂₀-alkylcarbonyl and are linked via O, CO, OCO, OCOO or COO,

Y is a direct bond, O, S, COO, OCO, OCOO, CON(R) or N(R)CO, and

Z is a polymerizable group,

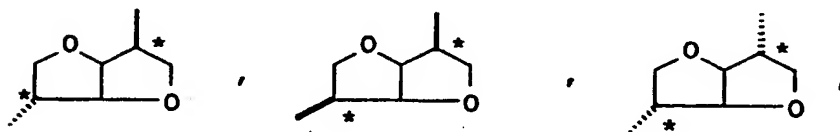
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m is 0 or 1,

n is from 2 to 6, and

X is a chiral radical of the formula

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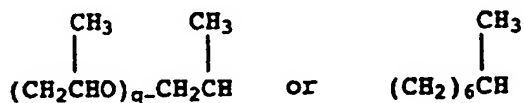
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R is C₁- to C₄-alkyl or hydrogen.

The spacer A can be any group known for this purpose; the spacers are usually linked to X via ester or ether groups or a direct bond. The spacers generally contain from 1 to 30, preferably from 1 to 12, carbon atoms and may be interrupted in the chain by, for example, O, S, NH or NCH₃. Suitable substituents for the spacer chain are fluorine, chlorine, bromine, cyano, methyl and ethyl.

Examples of representative spacers are the following:

10 (CH₂)_p, (CH₂CH₂O)_qCH₂CH₂,



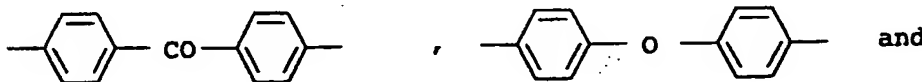
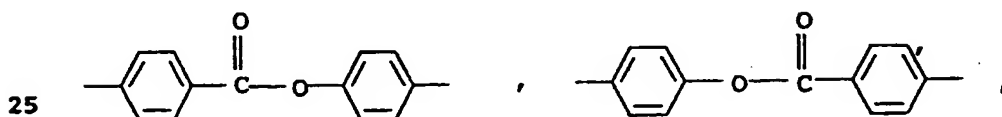
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where

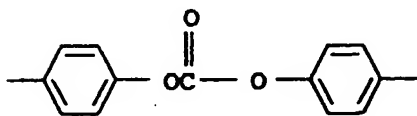
p is from 1 to 12, and

q is from 1 to 3.

20 Particularly preferred mesogenic groups M are, for example:



30



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The groups necessary for the novel compounds are linked to one another via bridges Y, such as O, S, COO, OCO, OCOO, CONH, NHCO, CON(R), N(R)CO or a direct bond, where R is C₁- to C₄-alkyl or hydrogen. Y is preferably O, OCO, COO or OCOO.

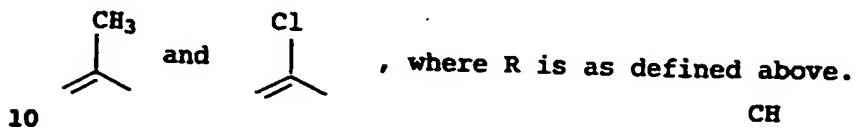
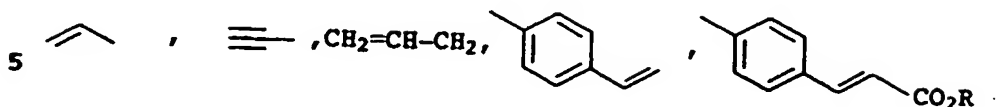
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n is preferably 2.

Polymerizable groups which may be mentioned in particular are vinyl radicals, which are present, for example, in acrylic

45 compounds, vinyl ethers and styrene derivatives. Epoxides are also suitable.

Examples of preferred radicals Z are the following:



, where R is as defined above.

Z is particularly preferably $\text{CH}_2=\text{CH}-$, $\text{CH}_2=\text{C}-$ or $\text{CH}_2=\text{C}(\text{CH}_3)-$.

15 The units $\text{Z}-\text{Y}[\text{A}]_m-\text{Y}-\text{M}-\text{Y}$ according to the invention, where Z, Y, m, A and M are as defined above, can be obtained by generally known synthetic methods, as described, for example, in EP-A 739403 and DE-A 39 17 196.

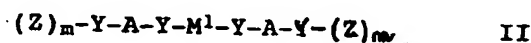
20 The chiral moieties can be purchased commercially and are thus available.

The novel compounds are suitable as high-twisting-power dopants for producing cholesteric liquid crystals. Using very small amounts, the reflection wavelength of the cholesteric mixture can be shifted into the visible region. It is advantageous here that the dopants form a stable mixture with the nematic host system, from which mixture the dopant does not crystallize out. The novel compounds are particularly suitable for this purpose.

30 The novel compounds are particularly suitable for use in electro-optical display elements or as chiral dopants for nematic or cholesteric liquid-crystal mixtures for producing layers which reflect in color.

35 The novel compounds are also suitable for use as chiral dopants in optical polarizers and optical filters.

Particular preference is given here to mixtures of the novel compounds with nematic compounds of the formula



where, in each case independently of one another, A, m, Y and Z are as defined above, and M^1 is a mesogenic group.

Compounds of the formula II are described, for example, in DE-OS 195 32 408, GB-A-22 79 659, (EP-A-749 466) and EP-A-648 827.

5 Also claimed are solid compositions comprising the novel compounds in copolymerized form.

Also claimed are solid compositions comprising the novel compounds and nematic compounds of the above formula II, in each
10 case in copolymerized form.

Solid compositions of this type may be, for example, polymers which can contain partly uncrosslinked or non-copolymerized constituents. Non-copolymerized constituents of this type can be,
15 for example, unreactive organic molecules having a wide variety of molecular weights or alternatively inorganic or organic pigments. They may furthermore also be additives, for example rheology auxiliaries or light and/or oxidation stabilizers.

20 It is of course also possible for solid compositions of this type to be the polymerization products of the claimed liquid-crystalline mixtures containing the novel compounds, and of the claimed liquid-crystalline mixtures containing nematic compounds of the above formula II in addition to the novel compounds.

25

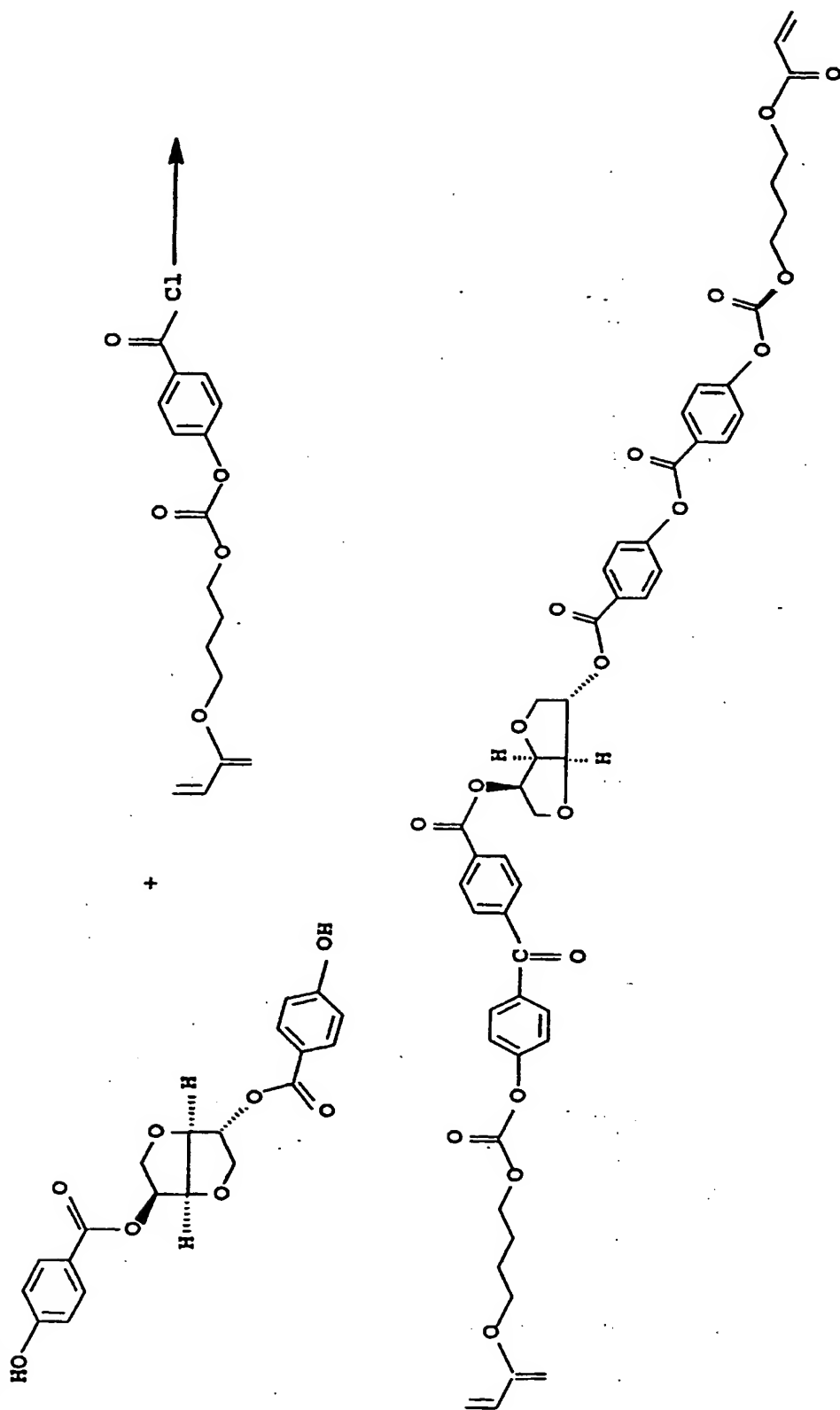
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Example 1



Procedure:

3.84g (0.01 mol) of bis(4'-hydroxybenzoyl)-1,4:3,6-dianhydrosorbitol are dissolved in 30 ml of DMF and 5.08 g (0.04 mol) of N,N-dimethylcyclohexylamine, and 8.0 g (0.024 mol) of 4-acryloxybutoxycarbonyloxybenzoyl chloride are then added dropwise at 0 - 5°C. The mixture is stirred at 0-5°C for one hour, at 40°C for 3 hours and then at RT overnight. The reaction mixture is poured into water and acidified using conc. hydrochloric acid. Ethyl acetate is added, and the organic phase is washed with water, dried over sodium sulfate and evaporated in a rotary evaporator.

Yield: 11.3 g

The crude product is chromatographed over 1.1 kg of silica gel using the eluent petroleum ether/ethyl acetate (2:1).

Yield: 9.3 g (96%) [NMR]

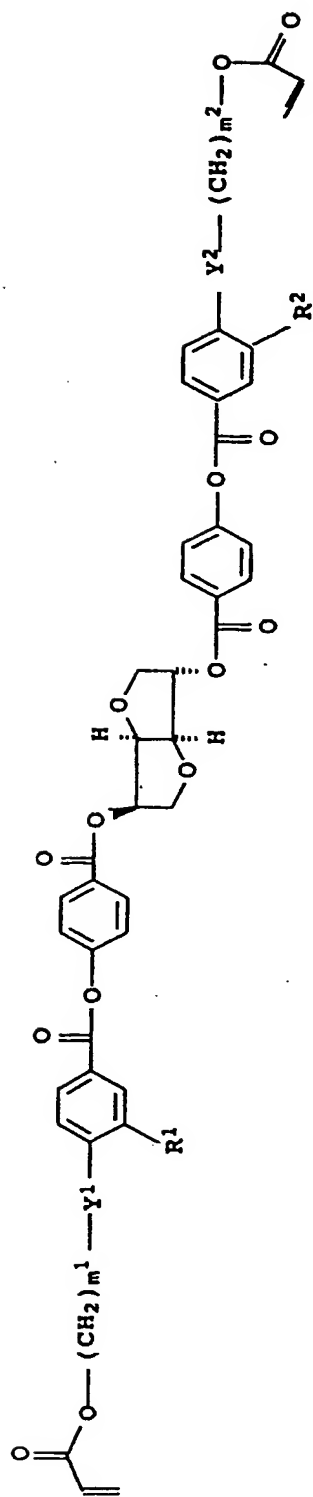
HTP in ZLI 1840 63 μm^{-1}

Melting point: 109°C (DTA)

The compound has a right-handed twist.

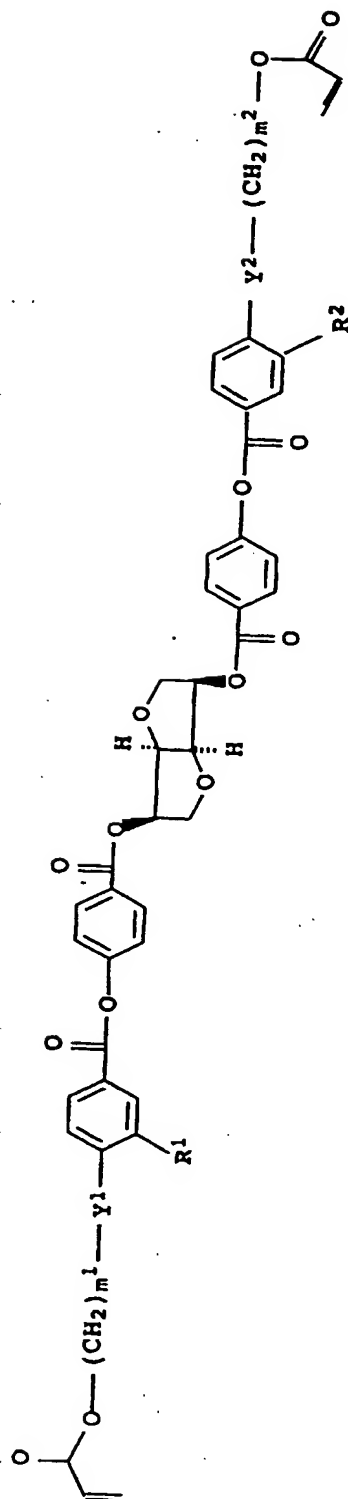
Further compounds prepared by this and similar processes are the following:

HTP = helical twisting power

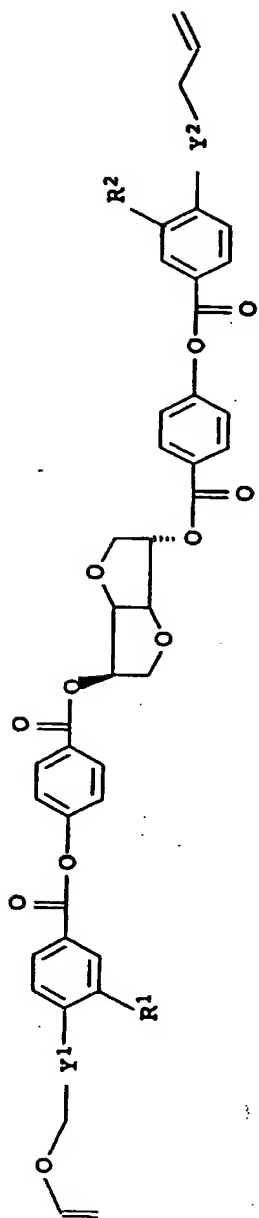


Ex.	Y ¹	Y ²	R ¹	R ²	m ¹	m ²	HTP ¹ μm-1 in ZLI 1840	Twist
2	OCOO	OCOO	OMe	OMe	2	4		right-handed
3	OCOO	OCOO	OMe	OMe	4	4	50	right-handed
4	OCOO	OCOO	OMe	OMe	6	6		right-handed
5	OCOO	OCOO	OMe	OMe	4	6		right-handed
6	OCOO	OCOO	OMe	OMe	6	4		right-handed
7	OCOO	OCOO	H	H	2	2		right-handed
8	OCOO	OCOO	H	H	4	2		right-handed
9	OCOO	OCOO	H	H	2	4		right-handed
10	OCOO	OCOO	H	H	6	6		right-handed
11	OCOO	OCOO	H	H	6	4		right-handed
12	O	O	H	H	2	2		right-handed
13	O	O	H	H	4	2		right-handed
14	O	O	H	H	4	4	63	right-handed
15	O	O	H	H	4	6		right-handed
16	O	O	H	H	6	6		right-handed
17	OCOO	O	H	H	4	4		right-handed
18	O	OCOO	H	H	4	4		right-handed
19	OCOO	O	H	H	6	6		right-handed

Ex.	Y ¹	Y ²	R ¹	R ²	m ¹	m ²	HTP μm-1 in ZLI 1840	Twist
20	O	OCOO	H	H	6	6		right-handed
21	OCO	COO	H	H	4	4		right-handed
22	OCO	COO	H	H	6	6		right-handed
23	OCO	O	H	H	4	4		right-handed
24	OCO	O	H	H	6	6		right-handed



Ex.	Y ¹	Y ²	R ¹	R ²	m ¹	m ²	HTP μm ⁻¹ in ZLI 1840	Twist
25	OCOO	OCOO	OMe	OMe	4	4	11	left-handed
26	OCOO	OCOO	OMe	OMe	6	6		left-handed
27	OCOO	OCOO	OMe	OMe	2	2		left-handed
28	O	O	H	H	2	2		left-handed
29	O	O	H	H	4	2		left-handed
30	O	O	H	H	4	4	63	left-handed
31	O	O	H	H	6	6		left-handed
32	COO	OCO	H	H	2	2		left-handed
33	COO	OCO	H	H	4	4		left-handed
34	COO	OCO	H	H	6	6		left-handed
35	COO	OCO	H	H	6	4		left-handed
36	OCOO	OCOO	H	H	2	2		left-handed
37	OCOO	OCOO	H	H	2	4		left-handed
38	OCOO	OCOO	H	H	4	4	13	left-handed
39	OCOO	OCOO	H	H	6	6		left-handed
40	OCOO	OCOO	H	H	4	6		left-handed
41	OCOO	OCOO	H	H	6	4		left-handed
42	O	O	OMe	OMe	4	4		left-handed

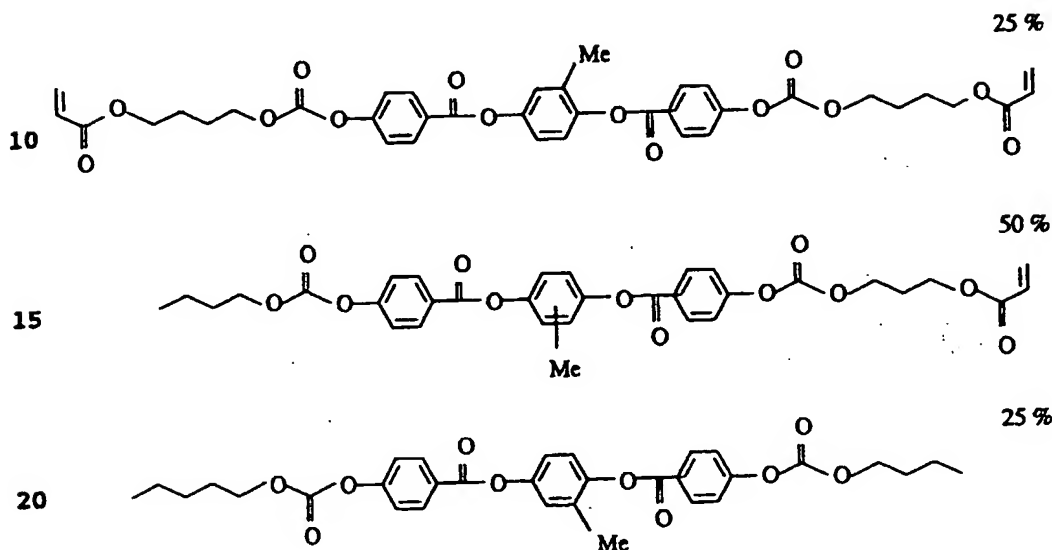


Ex.	Y1	Y2	R1	R2
43	O	O	H	H
44	O	O	OMe	OMe
45	O	O	Me	Me
46	OCOO	OCOO	H	H
47	OCO	OCO	H	H
48	OCO	OCO	H	H

Mixtures with liquid-crystalline substances

Example 49

5 x mol% of Example 1 are dissolved in the nematic mixture



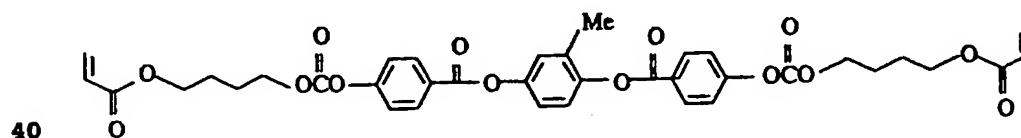
by mixing the melts. After cooling to RT, cholesteric phases with the following reflection wavelengths - depending on X - are obtained:

x (mol%)	λ_{\perp} (nm)
2.0	701
3.0	482
4.0	341

Example 50

x mol% of Example 1 are dissolved in the nematic compound

35



by mixing the melts. After cooling to RT, cholesteric phases with the following reflection wavelengths are obtained:

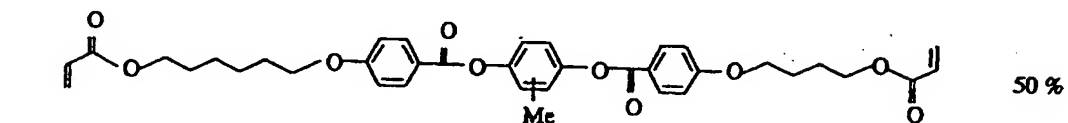
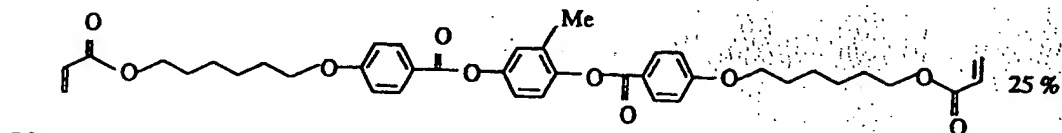
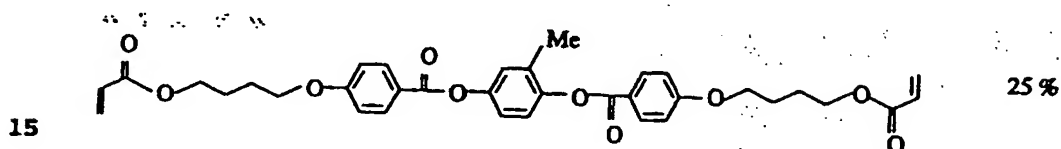
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x (mol%)	λ_{\perp} (nm)
3.05	660
3.51	565
5 4.28	465
5.46	365

Example 51

x mol% of Example 1 are dissolved in the nematic mixture

10



by mixing the melts. After cooling to RT, cholesteric phases with the following reflection wavelengths - depending on X - are obtained:

30

x (mol%)	λ_{\perp} (nm)
2.0	854
2.5	696
3.0	575
35 3.5	498

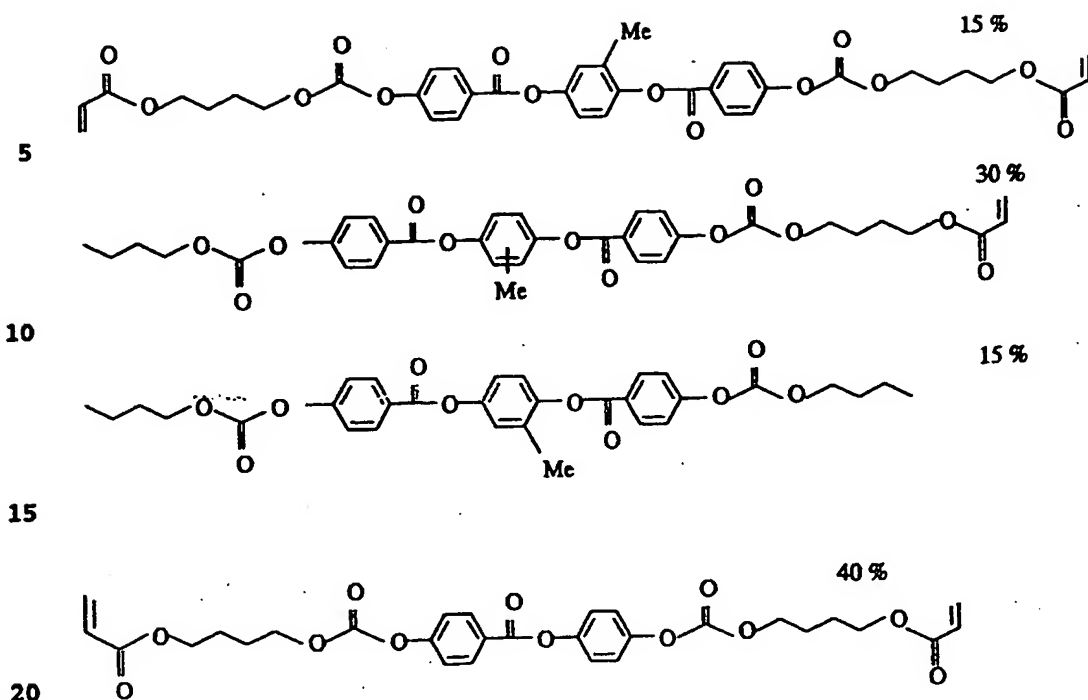
Example 52

x mol% of Example 1 are dissolved in the nematic mixture

40

45

15



by mixing the melts. After cooling to RT, cholesteric phases with the following reflection wavelengths - depending on X - are obtained:

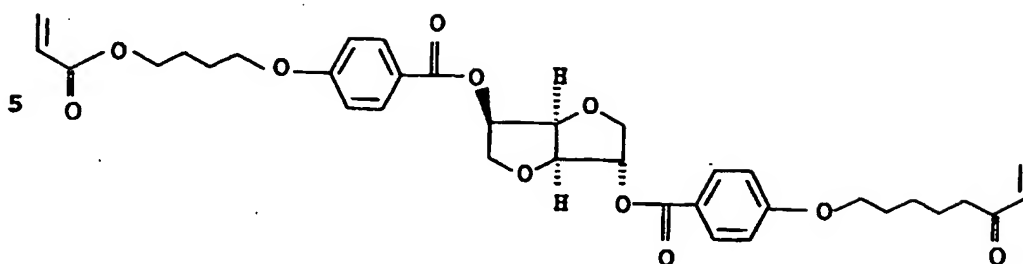
x (mol%)	λ_{\perp} (nm)
1.5	974
2.0	736
30 2.5	588
3.0	493

Comparative Example 53

35 4 mol% of both the compound from Example 1 and the compound of the formula III (corresponding to EP-A-739 403)

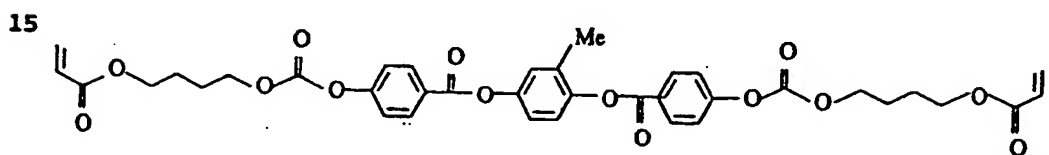
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III

are added to the nematic compound

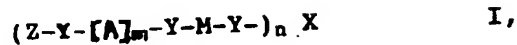


The two substances are melted and their spectrum measured at RT. The compound from claim 1 gives a reflection at 431 nm, while the compound of Formula III gives a reflection at 1087 nm.

Claims

1.- A compound of the formula

5



where, independently of one another,

10 A is a spacer,

M is a mesogenic group containing two phenylene radicals which are unsubstituted or substituted by C₁- to C₄-alkyl, methoxy, ethoxy, fluorine, chlorine, bromine, C₁- to C₂₀-alkoxycarbonyl or C₁- to C₂₀-alkylcarbonyl and are linked via O, CO, OCO, OCOO or COO,

15

Y is a direct bond, O, S, COO, OCO, OCOO, CON(R) or N(R)CO, and

Z is a polymerizable group,

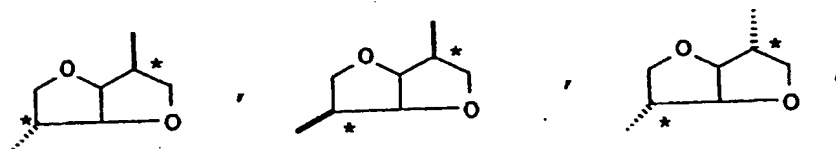
m is 0 or 1,

20

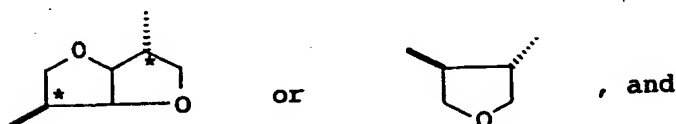
n is from 2 to 6, and

X is a chiral radical of the formula

25



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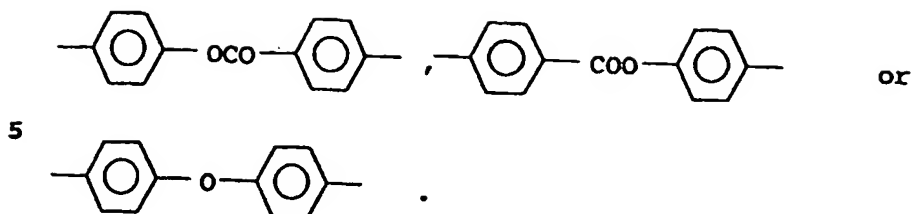
35 R is C₁- to C₄-alkyl or hydrogen.

2. A compound as claimed in claim 1, where n = 2.

3. A compound as claimed in claim 1, where M is

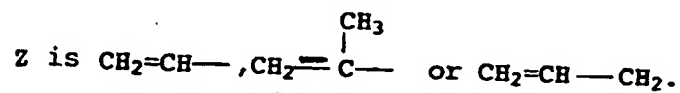
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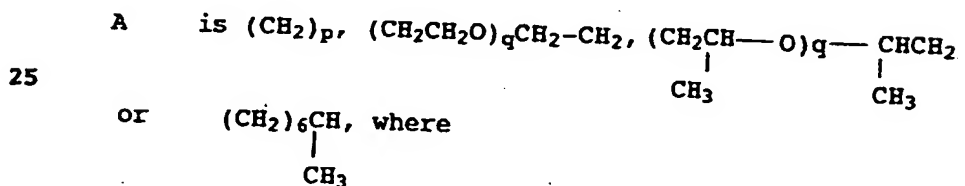
10 4. A compound as claimed in claim 1, where
 Y is O, OCO, COO, OCOO or a direct bond.

15 5. A compound as claimed in claim 1, where



20

6. A compound as claimed in claim 1, where

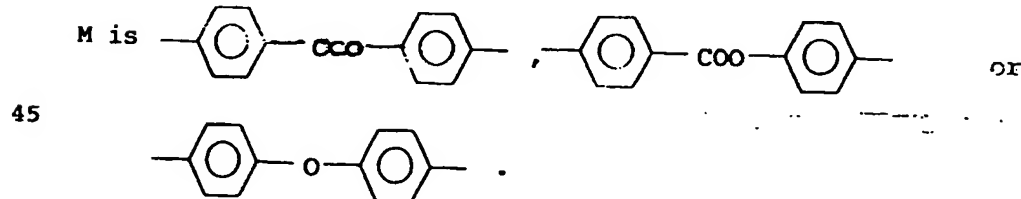
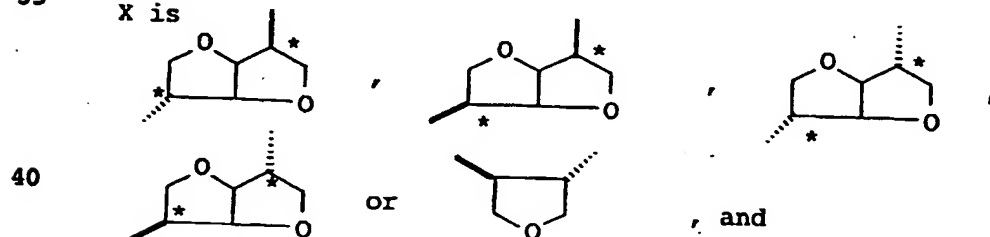


30 P is from 1 to 12 and q is from 1 to 3.

7. A compound as claimed in claim 1, where

35

X is



8. A compound as claimed in claim 1 and referred to in any of the foregoing Examples 1 to 52.
9. A liquid-crystalline mixture comprising one or more compounds as claimed in any of claims 1 to 8.
- 5 10. A liquid-crystalline mixture comprising one or more compounds as claimed in any of claims 1 to 8 and one or more nematic compounds of the formula II
- II
 $(Z)_m-Y-A-Y-M^1-Y-A-Y-(Z)_n$,
- 10 where, in each case independently of one another, A, m, Y and Z are as defined in claim 1, and M^1 is a mesogenic group.
11. A solid composition comprising a compound as claimed in any of claims 1 to 8 in copolymerized form.
12. A solid composition comprising a compound as claimed in any of claims 1 to 8 and a nematic compound of the formula II defined in claim 10, in each case in copolymerized form.
- 15
13. The use of a compound as claimed in any of claims 1 to 8 in electro-optical displays or as a chiral dopant for nematic or cholesteric liquid crystals for producing layers which reflect in color.
- 20
14. The use of a compound as claimed in any of claims 1 to 8 as a chiral dopant in optical polarizers and optical filters.



Application No: GB 9821817.5
Claims searched: 1-14

Examiner: Stephen Quick
Date of search: 8 January 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.Q): (not searched)

Int CI (Ed.6): (not searched)

Other: Online: CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	WO 95/16007 A1 (BASF), see pages 3 (lines 1-11), 4 (lines 40-end), 5 (lines 1-17) & 8 (lines 33-42); acknowledged in this application as EP 0739403	-

X Document indicating lack of novelty or inventive step
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- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
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- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
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